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(21) International Application Number: PCT/US94/05851 (22) International Filing Date: 26 May 1994 (26.05.94) (30) Priority Data: 08/072,015 7 June 1993 (07.06.93) US (71) Applicant: EASTMAN CHEMICAL COMPANY [US/US]; 100 North Eastman Road, Kingsport, TN 37660 (US). (72) Inventors: MILLS, David, Earl; 3112 Winesap Road, Kingsport, TN 37663 (US). STAFFORD, Steven, Lee; 161 Stafford Road, Gray, TN 37615 (US). CARICO, Joey, Carico; 203 Cedar Branch Road, Kingsport, TN 37664 (US). (74) Agent: THALLEMER, John, D.; P.O. Box 511, Kingsport, TN 37662-5075 (US).		(81) Designated States: BR, CA, CZ, HU, PL, RU, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published With international search report.
(54) Title: POLYESTER/ZEOLITE ADMIXTURES (57) Abstract This invention relates to a polyester/zeolite admixture having an excellent gas barrier property and an improved flavor retaining property, and clarity. More particularly, the present invention relates to a polyester/zeolite admixture wherein the zeolite is present in a critical amount of 100 parts per million (ppm) to 1,000 ppm. The present inventors have determined that addition of small- or medium-pore zeolites in a critical amount to a polyester reduces the concentration of acetaldehyde in the polyester without producing haze and thus improves the storage property, flavor retaining property, and fragrance retaining property of containers made from such polyester.		

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POLYESTER/ZEOLITE ADMIXTURES**FIELD OF THE INVENTION**

5 This invention relates to a polyester/zeolite
admixture having an excellent gas barrier property and
an improved flavor retaining property, and clarity.
More particularly, the present invention relates to a
polyester/zeolite admixture wherein the zeolite is
10 present in a critical amount of 100 parts per million
(ppm) to 1000 ppm. The present inventors have
determined that addition of small- or medium-pore
zeolites in a critical amount to a polyester reduces the
concentration of acetaldehyde in the polyester without
producing haze and thus improves the storage property,
15 flavor retaining property, and fragrance retaining
property of containers made from such polyester.

BACKGROUND OF THE INVENTION

20 Polyesters such as polyethylene terephthalate (PET)
are widely used for the production of light weight
plastic articles since PET is excellent in mechanical
properties such as formability and creep resistance and
can be biaxially molecularly oriented. However, during
molding or extrusion processes, acetaldehyde is formed
25 by thermal decomposition of the polyester and when the
polyester is formed into an article, the acetaldehyde in
the article walls migrates into the contents of the
article. Small amounts of acetaldehyde adversely affect
the flavor retaining property of foods and beverages,
30 and the fragrance retaining property of foods,
beverages, cosmetics, and other package contents. For
these reasons, it is desirable to minimize the migration
of acetaldehyde into package contents.

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The use of zeolites in polyesters is disclosed in U.S. Pat. Nos. 3,876,608, 4,391,971 and 5,104,965, and PCT International Publication No. WO 90/03408.

5 U.S. Pat. No. 3,876,608 discloses the addition of 13X or 4A zeolite in polyesters as a inert filler to increase surface roughness of polyester films. In this disclosure, the molten polymer film is contacted with a cooling quench drum to obtain amorphous polymer prior to biaxial orientation. Acetaldehyde is not mentioned.

10 U.S. Pat. No. 4,391,971 discloses a method for reducing the acetaldehyde content in PET by passing the PET through a bed of zeolite pellets. In this disclosure, the zeolite is not admixed with the polyester.

15 U.S. Pat. No. 5,104,965 discloses a process for preparing a crystalline polyethylene terephthalate which contains greater than 1000 ppm of a zeolite. No mention is made of acetaldehyde or haze. In contrast, the present inventors have determined that a
20 polyester/zeolite admixture wherein the zeolite is present in a critical amount of 100 parts per million (ppm) to 1000 ppm imparts adequate reduction in residual acetaldehyde without imparting haze to the polyester. If smaller than 100 ppm of zeolite is used, an
25 acceptable level of haze can be achieved, however, residual acetaldehyde is very large. On the other hand, if larger amounts of zeolite is used, residual acetaldehyde can be reduced but only at the expense of haze.

30 PCT International Publication No. WO 90/03408 discloses a process for making oriented PET film containing zeolites as slip additives. The use of zeolites as polymerization catalysts in PET is also disclosed. No mention is made of bottle or sheet

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applications, only oriented film primarily for magnetic tape applications. Acetaldehyde was not mentioned.

SUMMARY OF THE INVENTION

5 It is therefore an object of the present invention to reduce acetaldehyde contained in a polyester and improve the flavor retaining property and fragrance retaining property of contents in a vessel formed from the polyester without imparting haze to the polyester.

10 Another object of the invention is to provide polyester/zeolite admixtures which exhibit excellent mechanical properties such as impact resistance, stress crack resistance and heat resistance, and which display excellent melt flowability at the time of molding
15 thereof, and to provide processes for preparing said polyester/zeolite admixture.

 These and other objects are accomplished herein by a polyester/zeolite admixture having improved flavor retaining properties and clarity comprising:

20 (1) a polyester which comprises

 (a) a dicarboxylic acid selected from the group consisting of aromatic dicarboxylic acids, saturated aliphatic dicarboxylic acids, cycloaliphatic dicarboxylic acids, and combinations thereof, and

25 (b) a diol component comprising repeat units from at least 50 mole percent ethylene glycol, based on 100 mole percent dicarboxylic acid and 100 mole percent diol; and

 (2) 100 ppm to 1000 ppm of a zeolite selected from
30 the group consisting of small-pore zeolites and medium-pore zeolites.

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DESCRIPTION OF THE INVENTION

The polyester, component (1), of the present invention includes copolyesters. The polyester may be crystalline, semi-crystalline or amorphous. The polyester contains repeat units from a dicarboxylic acid and a diol, based on 100 mole percent dicarboxylic acid and 100 mole percent diol. Dicarboxylic acids useful in the present invention include aromatic dicarboxylic acids preferably having 8 to 14 carbon atoms, saturated aliphatic dicarboxylic acids preferably having 4 to 12 carbon atoms, and cycloaliphatic dicarboxylic acids preferably having 8 to 12 carbon atoms. Specific examples of dicarboxylic acids are: terephthalic acid, phthalic acid, isophthalic acid, naphthalene-2,6-dicarboxylic acid, cyclohexanedicarboxylic acid, cyclohexanediacetic acid, diphenyl-4,4'-dicarboxylic acid, succinic acid, glutaric acid, adipic acid, azelaic acid, sebacic acid, and the like. The polyester may be prepared from two or more of the above dicarboxylic acids.

It should be understood that use of the corresponding acid anhydrides, esters, and acid chlorides of these acids is included in the term "dicarboxylic acid".

The diol component contains repeat units from at least 50 mole percent ethylene glycol. Examples of diol comonomers which can be included with ethylene glycol are cycloaliphatic diols preferably having 6 to 15 carbon atoms or aliphatic diols preferably having 3 to 8 carbon atoms. Specific diol comonomers are: diethylene glycol, triethylene glycol, 1,4-cyclohexanedimethanol, propane-1,3-diol, butane-1,4-diol, pentane-1,5-diol, hexane-1,6-diol, 3-methylpentanediol-(2,4), 2-methylpentanediol-(1,4), 2,2,4-trimethylpentane-diol-(1,3), 2-ethylhexanediol-(1,3), 2,2-diethylpropane-

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diol-(1,3), hexanediol-(1,3), 1,4-di-(hydroxyethoxy)-benzene, 2,2-bis-(4-hydroxycyclohexyl)-propane, 2,4-dihydroxy-1,1,3,3-tetramethyl-cyclobutane, 2,2-bis-(3-hydroxyethoxyphenyl)-propane, and
5 2,2-bis-(4-hydroxypropoxyphenyl)-propane. The polyester may be prepared from one or more of the above diols.

The polyester may also contain small amounts of trifunctional or tetrafunctional comonomers such as trimellitic anhydride, trimethylolpropane, pyromellitic
10 dianhydride, pentaerythritol, and other polyester forming polyacids or polyols generally known in the art.

For the purposes of the present invention, the preferred polyester composition contains a dicarboxylic acid component which consists essentially of repeat
15 units from terephthalic acid and a diol component which consists essentially of repeat units from ethylene glycol.

Polyesters useful as component (1) have an inherent viscosity of 0.4 to 1.5 dL/g. Preferably, the polyester
20 has an inherent viscosity of 0.6 to 1.2 dL/g as measured at 25°C. using 0.50 grams of polymer per 100 ml of a solvent consisting of 60% by weight phenol and 40% by weight tetrachloroethane. The polyester may be prepared by conventional polycondensation procedures well-known
25 in the art. Such processes include direct condensation of the dicarboxylic acid(s) with the diol(s) or by ester interchange using a dialkyl dicarboxylate. For example, a dialkyl terephthalate such as dimethyl terephthalate is ester interchanged with the diol(s) at elevated
30 temperatures in the presence of a catalyst.

The second component of the present invention is a zeolite. Zeolites are crystalline alumino-silicates with highly ordered crystalline structure. Cavities of a defined size are formed in the rigid,
35 three-dimensional network composed of SiO_4 - and

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AlO₄-tetrahedra. The lattice contains cavities of varying diameters, depending on the type of zeolite. A distinction is made between large-, medium-, and small-pore zeolites. In the case of large-pore Y-zeolites, for example, a cavity of this type having a diameter of 7.4 angstroms is formed by twelve SiO₄ tetrahedra. In the case of small-pore A-zeolites, eight tetrahedra form a ring of diameter 4.1 angstroms. The medium-pore pentasil zeolites have a 10-ring system with an ellipsoidal tubular diameter of 5.5 angstroms x 5.6 angstroms. All medium-pore zeolites are pentasil zeolites which contain uniform channels. Small-pore and medium-pore zeolites are suitable for use in this invention. Examples of small-pore zeolites include A-zeolites such as 3A, 4A, and 5A, mordenite (small-pore type) such as AW-300 and ZEOLON-300 which are available from Union Carbide and Norton Company, erionite, chabazite, zeolite F such as IONSIV F80, and zeolite W such as IONSIV W85. IONSIV F80 and W85 are available from Union Carbide. Examples of medium-pore zeolites include ZSM-5, ZSM-11, ZSM-22, NU-10, Theta 1, ZSM-23, ZSM-48, TS-1, and silicalite.

The present inventors have determined that addition of small- or medium-pore zeolites in the range of 100 to 1000 ppm to the polyester, component 1, reduces the concentration of acetaldehyde in the polyester without producing haze and thus improves the storage property, flavor retaining property, and fragrance retaining property of containers made from such polyester.

The polyester compositions of this invention are prepared by mixing a polyester with small- or medium-pore zeolites. The zeolites can be readily incorporated into the polyester during the polymerization of the polyester or in a later step by any suitable mixing process such as batch mixing,

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single screw, or twin screw extrusion. Preferably, the zeolite is added during polymerization since this method produces less haze than melt blending. Because zeolites can absorb and release large amounts of water and hence contribute to polymer hydrolysis on melt blending, it is preferable to dehydrate the zeolites by heating to a temperature of greater than 350°C. before adding the zeolites to the polyester melt.

This invention is useful for various packaging applications. Examples include, but are not limited to, thermoformed or injection molded trays, thermoformed or injection molded cups, extrusion blow molded bottles, injection stretch blow molded bottles, extruded film, and extruded sheet.

The materials and testing procedures used for the results shown herein are as follows:

Acetaldehyde generation (AA Gen) was determined by the following method. After crystallizing for 30 minutes at 180°C., the pelletized polyester/zeolite admixture was dried overnight at 120°C. in a vacuum oven. A Tinius-Olsen melt indexer was loaded with 5 grams of the polyester or copolyester and held at the test temperature (preferably 275-310°C.) for five minutes. The molten polyester was extruded into water and stored at a temperature of -25°C. until grinding. The sample was ground to 20 mesh or finer and 0.5 grams was placed in a sample tube which was immediately sealed. The sample was analyzed by dynamic headspace gas chromatographic analysis using a Hewlett-Packard 5890 Gas Chromatograph with a Perkin Elmer Automatic Thermal Desorption ATD-50 as the injection system. Acetaldehyde was desorbed by heating the sample at 150°C. for ten minutes. The gas chromatography column had a 30 m by 0.53 mm inside diameter.

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Haze was determined by ASTM D1003. Haze values of less than 10% are acceptable for high quality packaging.

5 The invention will be further illustrated by a consideration of the following examples, which are intended to be exemplary of the invention. All parts and percentages in the examples are on a weight basis unless otherwise stated.

10

EXAMPLES 1-14

Poly(ethylene terephthalate) was prepared by the following procedure.

15 Dimethyl terephthalate, 145.5 grams, and 93.0 grams of ethylene glycol were placed in a polymerization reactor along with titanium tetraisopropoxide (20 ppm Ti), manganese acetate (55 ppm Mn), antimony oxide (225 ppm Sb), and cobalt acetate (75 ppm Co). The amount and type of zeolite indicated in Table I was also added. The mixture was heated with stirring under nitrogen
20 atmosphere at 200 °C. for 60 minutes, followed by 220 °C. for 60 minutes at which time ZONYL A, (120 ppm phosphorus) which is available from DuPont, was added. The reaction temperature was increased to 285 °C. and pressure was reduced to 0.3 torr. When the polymer
25 viscosity reached the desired level, the polymerization was terminated by removing the heat source and venting the reactor to ambient pressure. The resulting polyesters had inherent viscosities of 0.50-0.68 dL/g. These polyesters were solid-state polymerized to an
30 inherent viscosity of 0.70-0.72 dL/g.

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TABLE I

EXAMPLE	ZEOLITE		AA GEN		HAZE
	(type)	(ppm)	275°C.	295°C.	(%)
5	1	NONE	5.4	13.4	4.43
	2	4A	4.3	11.3	7.25
	3	3A	4.6	12.1	6.20
	4	13X	6.2	16.6	8.11
	5	3A	4.4	13.0	8.43
10	6	ALUMINA	5.4	12.9	5.72
	7	3A	4.3	14.5	6.74
	8	SILICA	6.2	11.7	6.41
	9	ALUMINA	6.1	12.8	8.15
	10	4A	2.3	9.6	44.20
15	11	4A	3.6	11.2	4.34
	12	4A	3.4	8.4	7.48
	13	NONE	7.4	19.1	3.20
	14	4A	3.7	16.1	17.97

20

The results in Table I clearly indicate that addition of small- or medium-pore zeolites, as opposed to using large-pore zeolites such as 13X or similar inorganic materials such as alumina and silica, in the range of 100 to 1000 ppm to a polyester reduces the concentration of acetaldehyde in the polyester without producing an unacceptable level of haze. An unacceptable level of haze has been defined as being greater than 10%.

30

EXAMPLES 15-25

Poly(ethylene terephthalate) was prepared by the following procedure.

Bis(2-hydroxyethyl) terephthalate, 190.5 grams, was placed in a polymerization reactor along with antimony oxide (225 ppm Sb), cobalt acetate (65 ppm Co) and ZONYL A (80 ppm phosphorus). The amount and type of zeolite indicated in Table II was also added. The mixture was heated with stirring under nitrogen atmosphere to 285 C. and pressure was reduced to 0.3 torr. When the polymer viscosity reached the

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desired level, the polymerization was terminated by removing the heat source and venting the reactor to ambient pressure. The resulting polyesters had inherent viscosities of 0.57-0.62 dL/g. These polyesters were solid-state polymerized to an inherent viscosity of 0.70-0.72 dL/g.

TABLE II

EXAMPLE	ZEOLITE (type)	ZEOLITE (ppm)	AA GEN		HAZE (%)
			275°C.	295°C.	
15	NONE	—	2.7	10.5	2.34
16	NONE	—	3.7	12.9	3.28
17	4A	100	3.4	14.0	3.12
18	4A	250	2.3	14.1	3.04
19	4A	250	2.5	13.7	3.49
20	4A	500	2.5	13.3	8.03
21	4A	1000	2.5	13.6	10.47
22	4A	1000	2.3	15.7	6.51
23	4A	2000	2.1	11.4	13.54
24	4A	5000	1.7	10.9	40.18
25	NONE	—	3.2	13.0	2.74

The results in Table II clearly indicate that addition of small- or medium-pore zeolites in the range of 100 to 1000 ppm to a polyester reduce the concentration of acetaldehyde in the polyester without producing an unacceptable level of haze, as compared to polyester compositions without zeolites. The addition of small- and medium-pore zeolites to the polyester prepared using the catalyst system in Examples 1-14 have a greater effect in reducing the acetaldehyde than adding the same types of zeolites to the polyester used in Examples 15-25 which contain less catalyst metals.

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EXAMPLE 26

A polyester resin was prepared by mixing powdered 4A zeolite, 0.6 grams, with 599.4 grams of KODAPAK PET 9921W which is available from Eastman Chemical Company, and extruding/pelletizing in a Brabender extruder at 275°C. melt temperature. The zeolite was heated at 500°C. for 12 hours and the PET was dried at 150°C. for 12 hours. The pelletized polyester/zeolite resin was crystallized by heating at 180°C. for 30 minutes and dried in a vacuum oven for 12 hours at 120°C.

Acetaldehyde generation was 8.1 ppm at 275°C. and 18.1 ppm at 295°C. compared to 11.0 ppm at 275°C. and 25.5 ppm at 295°C. without the zeolite additive.

EXAMPLE 26

A polyester resin was prepared by mixing powdered 4A zeolite, 6.0 grams, with 594.0 grams of KODAPAK PET 9921W and extruding/pelletizing in a Brabender extruder at 275°C. melt temperature. The zeolite was heated at 500°C. for 12 hours and the PET was dried at 150°C. for 12 hours. The pelletized polyester/zeolite resin was crystallized by heating at 180°C. for 30 min and dried in a vacuum oven for 12 hours at 120°C.

Acetaldehyde generation was 6.7 ppm at 275°C. and 12.7 ppm at 295°C. compared to 11.0 ppm at 275°C. and 25.5 ppm at 295°C. without the zeolite additive.

Many variations will suggest themselves to those skilled in this art in light of the above detailed description. All such obvious modifications are within the full intended scope of the appended claims.

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WHAT IS CLAIMED IS:

1. A polyester/zeolite admixture having improved flavor retaining properties and clarity comprising:
 - (1) a polyester which comprises
 - (a) a dicarboxylic acid selected from the group consisting of aromatic dicarboxylic acids, saturated aliphatic dicarboxylic acids, cycloaliphatic dicarboxylic acids, and combinations thereof, and
 - (b) a diol component comprising repeat units from at least 50 mole percent ethylene glycol, based on 100 mole percent dicarboxylic acid and 100 mole percent diol; and
 - (2) 100 ppm to 1000 ppm of a zeolite selected from the group consisting of small-pore zeolites and medium-pore zeolites.
2. A polyester/zeolite admixture having improved flavor retaining properties and clarity comprising:
 - (1) a polyester which comprises
 - (a) a dicarboxylic acid component comprising repeat units from at least 85 mole percent terephthalic acid; and
 - (b) a diol component comprising repeat units from at least 85 mole percent ethylene glycol, based on 100 mole percent dicarboxylic acid and 100 mole percent diol; and
 - (2) 100 ppm to 1000 ppm of a zeolite selected from the group consisting of small-pore zeolites and medium-pore zeolites.
3. The polyester/zeolite admixture of Claim 1 wherein the polyester comprises a dicarboxylic acid consisting essentially of repeat units from terephthalic acid and a diol consisting essentially of repeat units from ethylene glycol.

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4. A heat-molded or draw-formed plastic article composed of a thermoplastic polyester/zeolite composition comprising:

(1) a polyester which comprises

5 (a) a dicarboxylic acid selected from the group consisting of aromatic dicarboxylic acids, saturated aliphatic dicarboxylic acids, cycloaliphatic dicarboxylic acids, and combinations thereof, and

(b) a diol component comprising repeat units from
10 at least 50 mole percent ethylene glycol, based on 100 mole percent dicarboxylic acid and 100 mole percent diol; and

(2) 100 ppm to 1000 ppm of a zeolite selected from the group consisting of small-pore zeolites and
15 medium-pore zeolites.

5. The plastic article according to Claim 4 wherein the dicarboxylic acid component consists essentially of repeat units from terephthalic acid, and the diol
20 component consists essentially of repeat units from ethylene glycol.

6. The polyester/zeolite admixture of Claim 1 wherein the small-pore zeolite is selected from the group
25 consisting of A-zeolites, erionite, chabazite, small-pore type mordenite, zeolite F, and zeolite W.

7. The polyester/zeolite admixture of Claim 6 wherein the A-zeolite is selected from the group consisting of
30 3A, 4A, and 5A.

8. The polyester/zeolite admixture of Claim 7 wherein the A-zeolite is 4A.

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- 5 9. The polyester/zeolite admixture of Claim 1 wherein the medium-pore zeolite is selected from the group consisting of ZSM-5, ZSM-11, ZSM-22, NU-10, Theta 1, ZSM-23, ZSM-48, TS-1, and silicalite.
- 10 10. The polyester/zeolite admixture of Claim 2 wherein the small-pore zeolite is selected from the group consisting of A-zeolites, erionite, chabazite, small-pore type mordenite, zeolite F, and zeolite W.
11. The polyester/zeolite admixture of Claim 10 wherein the A-zeolite is selected from the group consisting of 3A, 4A, and 5A.
- 15 12. The polyester/zeolite admixture of Claim 11 wherein the A-zeolite is 4A.
- 20 13. The polyester/zeolite admixture of Claim 2 wherein the medium-pore zeolite is selected from the group consisting of ZSM-5, ZSM-11, ZSM-22, NU-10, Theta 1, ZSM-23, ZSM-48, TS-1, and silicalite.
- 25 14. A process for preparing a polyester/zeolite admixture having improved flavor retaining properties and clarity comprising adding 100 ppm to 1000 ppm of a zeolite selected from the group consisting of small-pore zeolites and medium-pore zeolites to a polyester during the polymerization of the polyester, said polyester comprising
- 30 (a) a dicarboxylic acid selected from the group consisting of aromatic dicarboxylic acids, saturated aliphatic dicarboxylic acids, cycloaliphatic dicarboxylic acids, and combinations thereof, and

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(b) a diol component comprising repeat units from at least 50 mole percent ethylene glycol, based on 100 mole percent dicarboxylic acid and 100 mole percent diol.

INTERNATIONAL SEARCH REPORT

Int. Appl. No.
PCT/US 94/05851

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C08K3/34 C08L67/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 5 C08K C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	WO, A, 93 21264 (EASTMAN KODAK COMPANY) 28 October 1993 see page 5, line 6 - line 8 see page 6, line 29 - page 7, line 5; claims ---	1-8, 10-12, 14
X	WO, A, 92 18554 (EASTMAN KODAK COMPANY) 29 October 1992 see claims; example 1 ---	1-8, 10-12, 14
X	WO, A, 90 03408 (E.I. DUPONT DE NEMOURS AND COMPANY) 5 April 1990 cited in the application see page 3, line 3 - line 23; claims --- -/--	1-8, 10-12, 14

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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Date of mailing of the international search report

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,5 104 965 (WAYLON L. JENKINS ET AL.) 14 April 1992 cited in the application see claims ---	1-8, 10-12,14
X	CHEMICAL ABSTRACTS, vol. 107, no. 6, 10 August 1987, Columbus, Ohio, US; abstract no. 41111, see abstract & JP,A,62 070 442 (DIAFOIL CO., LTD) 31 March 1987 ---	1
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A	US,A,4 391 971 (FREDDIE L. MASSEY ET AL.) 5 July 1983 cited in the application see tables 1,2 -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 94/05851

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LU-A-67676	04-12-73	US-A- 3876608 BE-A- 800054 CA-A- 1023077 DE-A,C 2326862 FR-A,B 2189465 GB-A- 1427157 JP-C- 1222888 JP-A- 49042752 JP-B- 56049947 NL-A- 7307323	08-04-75 26-11-73 20-12-77 20-12-73 25-01-74 10-03-76 15-08-84 22-04-74 26-11-81 28-11-73
US-A-4391971	05-07-83	CA-A- 1197943	10-12-85